Study of CO₂ Absorption and Desorption in a Packed Column

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Carbon dioxide, a major greenhouse gas, may need to be removed from flue gas produced by combustion of fossil fuels in order to manage future climate changes. Although conventional wet scrubbing techniques exist for removal of carbon dioxide from gas streams, the wet scrubbing techniques must improve to process large volumes of flue gas at acceptable thermal efficiencies and minimal costs. Amine scrubbing is one such technique to remove CO2. To make the process more efficient, various areas of improvement were investigated: gas-liquid contacting area, the type of reactant, and dilution of the aqueous fraction with organic liquids. Pertaining to the former, various absorption tests with conventional packing material and structured packings were conducted with mono-ethanolamine (MEA), a traditional solvent, as well as with novel amines. Significant improvements in CO₂ removal were obtained with the structured packing. With respect to the amine investigation, a key to improved efficiency is the ease of regeneration of the CO₂loaded absorbent. Testing with a sterically hindered amine, 2-amino-2-methyl-1-propanol, revealed that, although absorption was somewhat less as compared to MEA, thermal regeneration was far easier. In addition, the effect of organic diluent on CO₂ absorption capacity of MEA solution is determined. The impact of various process parameters on the absorption and desorption steps will also be discussed.

Introduction

Chemical solvent absorption is based on reactions between CO2 and one or more basic absorbents, such as aqueous solutions of mono-, di-, or tri-ethanolamine. An advantageous characteristic of absorption is that it can be reversed by sending the CO2-rich absorbent to a desorber (or stripper) where the temperature is raised. In the case of physical absorption, where solvents include methanol, poly(ethylene glycol), dimethyl ether, and others, CO2 is absorbed under pressure, and the gas desorption can be achieved at reduced pressure. The regenerated absorbent is then returned to the absorber, thereby creating a continuous recycling process. The disadvantages of chemical absorption processes include their limited loadings and high energy requirements resulting from the reaction stoichiometry and the heats of absorption, respectively. There are also problems of corrosion and degradation.

All currently available CO_2 separation processes are energy intensive. In ranking the energy penalty of various capture processes, combustion with pure oxygen is the least energy intensive (about 30% energy penalty), and is followed by chemical solvent absorption processes (about 35% energy penalty). Also, it has been concluded that even the current most efficient technology will reduce energy efficiency of utility steam plants by about 30% and will increase the price of electricity by 80%,

even before disposal costs are added. These results are consistent with an EPRI study on CO_2 capture and disposal. Combustion with pure oxygen requires redesign of the entire combustion and boiler system, and therefore, cannot be retrofitted. The chemical solvent absorption process for CO_2 capture can be retrofitted in existing boiler systems and provides a rationale to pursue near-term evolutionary capture techniques. Emerging and future electricity generation technologies and novel CO_2 capturing methods have the potential to significantly reduce electricity costs if the control of CO_2 emissions is mandated.

In a more recent study,⁷ it has been projected that the energy penalty of amine scrubbing of flue gas

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(3) Booras, G. S.; Smelser, S. C. An Engineering and Economic Evaluation of CO_2 Removal from Fossil-Fired Power Plants. *Energy* **1991**, *16*, pp 1295–1305.

(4) Mimura, T. S.; Ijjima, M.; Mitsuoka, S. Development on Energy Saving Technology Saving Technology for Flue Gas Carbon Dioxide Recovery by Chemical Absorption Method and Steam System in Power Plant. *Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies*; Pergamon Press: Elmsford NY; Interlaken, Switzerland, Aug. 30—Sept. 2, 1988; pp 71—76.

⁽¹⁾ Aroonwilas, A.; Toniwachwuthikul, P. Mass Transfer of High Performance Structured Packing for CO₂ Separation Processes. *Proceedings of the 3rd International Conference on Carbon Dioxide Removal*; Pergamon Press: Elmsford, NY; Sept. 9–11, 1996, Cambridge, MA; pp S75–S80.

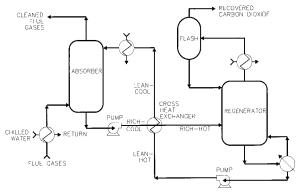


Figure 1. Flowsheet for the recovery of CO_2 from flue gas using chemical absorption.

produced in a coal-fired utility can be reduced to 15% through various improvements to the process. Some of these improvements other than process integration were outlined by Plasynski and Chen.⁸

Increased contacting areas per unit volume will enhance gas—liquid interactions and thus mass transfer. Regeneration of the spent amine solution is an energy-intensive step. As compared to conventional monoethanolamine (MEA), sterically hindered amines require lower heats of regeneration. In the MEA process, the aqueous fraction is about 80% of the solution, and during the regeneration step, this must be heated. Certain organic diluents have specific heats about 50% lower than water, and thus the possibility exists that replacing a portion of the water in the MEA solution with organic diluent may reduce the energy penalty during the regeneration heating cycle. It is the intent of the present study to investigate improvements in the amine scrubbing process for CO₂ capture.

Experimental Section

Absorption. Figure 1 shows amine scrubbing, a typical liquid chemical absorption process for CO2 capture. The flowsheet represents a continuous absorption/regeneration cycling process. CO2 is captured in the absorber at approximately 38 °C and is released from the regenerator at approximately 121 °C at a much higher CO₂ concentration. In the present investigation, the experimental apparatus consists of a packed-column absorber to promote gas-liquid contact and reaction in a counter-current flow pattern. Figure 2 shows the schematic diagram of the packed column absorber. The glass absorber is 7.6-cm i.d. and packing height varied from 18 to 71 cm during this series of tests. The reactor has an exterior jacket with hot water flowing in this outer jacket for absorber temperature control. The heat-jacketed section is 83 cm high. CO₂ absorbent enters from the top of the absorber through a spray nozzle to ensure good initial liquid

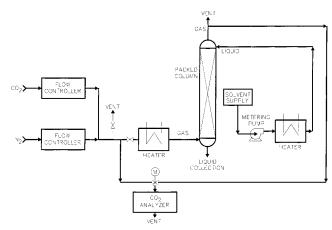


Figure 2. Simplified flowsheet for CO₂ scrubbing.

distribution to the packing material. The spray nozzle, which delivers fine mists, is placed 2.5 cm above the packing. The liquid is electrically preheated to the reactor control temperature in the stainless steel inlet line. The baseline absorber temperature is normally set at 38 °C during CO_2 absorption. Liquid flow rate is measured by a MicroMotion mass flowmeter, and controlled by a metering pump. Flow rate and temperature data are continuously stored in a computer at a predetermined time interval.

Simulated flue gas enters from the bottom of the absorber. Gas flow rate is controlled by a mass flow meter controller manufactured by Tylan General. Gas flow rate data are also stored in computer files. The baseline gas composition is 15% CO_2 and 85% N_2 . Coal-fired flue gas nominally consists of 15% CO_2 on a dry basis when the combustion takes place with 20% excess air. Sulfur oxides, hydrogen chloride, nitrogen oxides, and oxygen are not included in the simulated flue gas to avoid possible interferences with the test objectives for this series of experiments. These gases are known to cause degradation of the solvents.

The temperature of the experiment is maintained by controllers on the solvent inlet heater, the gas inlet heater, and the water jacket heater. For all of the tests described below, the temperature setpoints for these three streams are equivalent at each test condition. The actual temperatures typically vary from the setpoint by less the 0.5 °C. The gas temperature at the exit of the packing is measured at a point 1 cm above the solvent nozzle. It is generally greater than the gas inlet temperature due to the exothermic absorption; the magnitude of the temperature rise depends on the amount of CO₂ absorbed. During this series of tests, the temperature variations along the height of the packing were not measured owing to the cooling water flowing in the outer jacket of the double-jacketed packed-column reactor. The double jacket was designed to counter the exothermic heat of reaction between carbon dioxide and absorbents. In the future the temperature variation along the center core of the packing with and without the cooling water flowing in the outer jacket will be monitored.

The initial objectives of the experiments are (1) to obtain first-hand data on the effect of structured packing versus traditional random (or dumped) packing on the CO_2 capture rate; (2) to obtain CO_2 capture rate data by mono-ethanolamine (MEA) and by a sterically hindered amine; and (3) to compare CO_2 stripping rates between CO_2 -rich MEA and CO_2 -rich sterically hindered amine. The sterically hindered amine used during this test series was 2-amino-2-methyl-1-propanol (AMP). AMP reacts with CO_2 at a slower rate than MEA. Though AMP reacts with CO_2 at a slower rate, less energy is required to drive out CO_2 from its CO_2 -rich solution. There is a wide selection of sterically hindered amines. Recently, in Japan, Kansei Electric Power Company, in conjunction with Mitsubishi Heavy Industries Limited, has developed a sterically

⁽⁵⁾ Freon, P. H. M.; Jansen, A. E. Techno-economic assessment of membrane gas absorption of the production of carbon dioxide from flue gas. *Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies*; Pergamon Press: Elmsford, NY; Interlaken, Switzerland, Aug. 30—Sept. 2, 1998; pp 53—58.

⁽⁶⁾ Chakma, A. CO₂ Capture Processes—Opportunities For Improved Energy Efficiencies. *Proceedings of the 3rd International Conference on Carbon Dioxide Removal*; Pergamon Press: Elmsford, NY; Cambridge, MA, Sept. 9–11, 1996; pp S51–S56.

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(7) Herzog, H.; Drake, E.; Adams, E. CO₂ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change. DOE Final Report DE-AF22-96PC01257; January 1997.

(8) Plasynski, S. I.; Chen, Z.-Y. Review of CO₂ Capture Technologies of CO₂ Capture Technologies of CO₃ Capture Technologies of CO₄ Capture Technologies of CO₅ Capture T

⁽⁸⁾ Plasynski, S. I.; Chen, Z.-Y. Review of CO₂ Capture Technologies and Some Improvement Opportunities. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* August 2000, *45*, (4), 650–655.

hindered amine specifically for CO₂ recovery from flue gas.⁴ TNO, in The Netherlands, also is developing liquid absorbents for flue gas applications.⁵ However, the identities of those absorbents were not disclosed.

The basic reaction chemistry for an aqueous monoethanolamine solution and CO_2 is represented by the following reversible reaction:²

$$\textbf{C}_2\textbf{H}_4\textbf{OH}~\textbf{N}\textbf{H}_2 + \textbf{C}\textbf{O}_2 + \textbf{H}_2\textbf{O} \xrightarrow[\textbf{Hot}]{\textbf{Cold}} \textbf{C}_2\textbf{H}_4\textbf{OH}\textbf{N}\textbf{H}_3^{\ +} + \textbf{H}\textbf{C}\textbf{O}_3^{\ -}$$

This is an exothermic reaction and 72 KJ of thermal energy is released per mole of CO_2 absorbed in MEA solution. Absorption usually takes place near 50 °C. During regeneration, thermal energy (about 165 kJ/mole of CO_2) is added to the solution to release the CO_2 , because a large amount of water in the 20 wt % amine solution must be heated to regeneration temperature. Regeneration usually takes place near 120 °C. It has been estimated that up to 80% of total cost in the CO_2 absorption/regeneration cycle is due to the regeneration procedure.

Three types of column packings are compared for their CO_2 absorption rates at identical test conditions: Intalox saddle (ceramic, random packing), 1.9-cm and the smallest available from the supplier (Norton Chemical Process Products); Flexipac structured packing supplied by Koch Engineering Company; and BX Gauze structured packing also supplied by Koch Engineering Company. Structured packing provides more gas—liquid contact surface area per unit packed volume than random packings. Thus the overall CO_2 capturing capacity and rate by the liquid absorbent is increased. The packing height ranged approximately 18 cm to 71 cm during this series of tests.

 ${\bf CO_2}$ **Absorption Rate Determination.** Inlet nitrogen flow, inlet ${\bf CO_2}$ concentration (vol %), and outlet ${\bf CO_2}$ concentration (vol %) are used to calculate instantaneous absorption rates every 10 s during an absorption test. The nitrogen flow is measured by a mass flow controller. The inlet and outlet ${\bf CO_2}$ concentrations are measured by an Horiba infrared gas analyzer, which is calibrated immediately before the test. The inlet ${\bf CO_2}$ flow rate is calculated using the following equation:

$$G_{i} = [(F \times D/M)/(1 - y_{i})]y_{i}$$
 (1)

where $G_i = CO_2$ inlet flow rate (lb-mol/h), F = nitrogen gas flow rate (ft³/h), D = density of nitrogen (lb/ft³) at standard conditions, M = molecular weight of nitrogen, and $y_i = CO_2$ mole fraction at inlet of absorber (vol %).

The inlet CO_2 concentration, y_i , is averaged for the 20 data points (190 s) recorded immediately before solvent flow is initiated and is assumed constant throughout the test duration. The CO_2 inlet flow rate is controlled by a mass flow controller. The calculated flow rate, G_i , is used in the absorption calculation for data accuracy purposes. Since nitrogen gas is inert in the absorber, the outlet CO_2 flow rate is calculated using the nitrogen flow rate and outlet CO_2 concentration using the following equation:

$$G_0 = [(F \times D/M)/(1 - y_0)]y_0 \tag{2}$$

where $G_0 = \text{CO}_2$ outlet flow rate(lb-mol/h), and $y_0 = \text{CO}_2$ mole fraction at outlet of absorber (vol %).

The CO_2 absorption rate is the difference between the inlet and outlet CO_2 flow rates. Total CO_2 absorbed in the absorber can be obtained by integrating the instantaneous rates over a selected time period. Efficiency of CO_2 absorption is defined as $[(y_i-y_o)/y_i]\times 100\%$ at steady state.

Regeneration. The CO_2 -rich liquid chemical absorbent can be regenerated by heating. CO_2 evolves from the rich liquid absorbent during the heating. This regenerated liquid absorbent is CO_2 -lean and recirculated to the absorber for reuse in

Table 1. Absorber Efficiency and Absorbent/CO₂

Molar Ratio^a

mola rati		packing	absorbent utilization, %	
1.4	61.5 ± -0.7	BX gauze	43.9 ± 0.5	
2.2	98.1 ± 0.8	BX gauze	43.6 ± 0.6	
1.4	41.4	Flexipac	29.6	
1.4	40.1	Random Saddle	28.6	

 a Absorbent: 20 wt % MEA; absorber temp: 38 °C; molar ratio: mole absorbent inlet/mole CO2 inlet; absorber height: 53 cm.

an actual process. The regeneration temperature is usually set at 121 °C under slightly elevated pressure in the carbon dioxide industry. In the present investigation, the uniqueness of the laboratory reactor is that the absorber was used as the regenerator during the regeneration phase of the absorption/ regeneration cycle. The only difference is that higher temperature is maintained in the packed column in order to drive away CO2 from the rich amine solution. The structured packing accelerates the CO₂ release from the CO₂-rich amine solution. Prior to regeneration, the amine solution is saturated with CO₂. The CO₂-rich solution, which is sprayed into the reactor, is trickling in a thin film down the extensive surface area provided by the packing. No purge gas is required during the regeneration; the recovered CO₂ is pure after condensing out the vapor. A bag meter is used to measure the total mass of CO2 evolving from a known amount of CO2-rich amine solution; the time at every 2830 cm³ (0.1 ft³) advance at the bag meter is manually recorded.

Evaluation of Organic Diluent. The purpose of using organic diluent to replace some portions of water in the amine solution is to reduce the thermal energy required to heat the CO₂-saturated absorbent. If part of the water is replaced by an organic diluent, an amount of thermal energy could be saved during the solvent heating cycle for releasing CO₂. Two organic diluents, methanol and ethylene glycol, were studied. Methanol has a density of 0.79 g/mL and a normal boiling point of 64.7 °C; ethylene glycol has a density of 1.11 g/mL and a normal boiling point of 198 °C.

Results and Discussions

Absorber Efficiencies. Effects of absorbent (MEA) flow rate and packing type on CO_2 absorption efficiencies are compared. The test results are shown in Table 1. Higher absorbent flow rate increases CO_2 absorption efficiency as expected. Absorbent utilization is defined as the removal efficiency divided by the stoichiometric ratio. If 1 mole of MEA has a maximum capacity in removing 1 mole of CO_2 , the stoichiometric ratio of MEA to CO_2 is equal to the mole ratio divided by 1.

Three types of packings were studied for their effectiveness in CO_2 absorption: BX wire gauze, Flexipac 1Y, and random saddle (ceramic 0.95 cm) packings. BX gauze and Flexipac structured packings are the products of Koch Engineering Company. The specific surface area for BX Gauze, Flexipac, and random packings are 500, 400, and 66 m²/m³, respectively. At an absorbent-to- CO_2 mole ratio of 1.4, BX gauze improves packed column absorber efficiency by about 50% over the use of random saddle packing. Flexipac minimally improved efficiency over random saddle packing. Also, the increase in molar ratio increases the removal efficiency. The variability in the calculated efficiencies is approximately \pm 0.8%.

Comparison of CO₂ Absorption Rates. Table 2 shows that the sterically hindered amine, AMP, attained near-equal CO_2 absorption rate using structured packing as compared to random saddle packing for MEA

Table 2. Packing Type and Absorbent Effects on CO₂
Absorption Rate^a

CO_2 absorption rate, kg-mol/s $\times~10^6$	absorbent	packing
2.65	MEA	BX gauze
1.78	MEA	Random Saddle
1.88	AMP	BX gauze
1.23	AMP	Flexipac
1.15	AMP	Random Saddle

 $[^]a$ Absorbent: 20 wt % MEA; absorber temp: 38 °C; absorbent: 29.2 wt % AMP; absorber height: 53 cm; molar ratio 1.4 (for both MEA and AMP).

Table 3. Rate of CO₂ Regeneration, AMP versus MEA^a

	MEA (20 wt %)	AMP (29.25 wt %)	CO ₂ regeneration rate ratio AMP/MEA
CO ₂ regeneration rate, kg-mol/s × 10 ⁶	0.56	1.03	1.83
regeneration temp °C	93	93	N/A
CO ₂ saturated absorbent flow. lb/h	10.7	10.7	NA

^a Structured packing height: 53 cm (BX gauze).

processing. In these tests, 29.2 wt % of AMP solution is used while only 20 wt % of MEA solution is used, because the molecular weight of AMP is larger than MEA. Thus equal molar flowrates (0.09 lb-mol/h) are maintained for both MEA and AMP in the absorbent solution, respectively. Flexipac structured packing did not significantly improve the CO_2 absorption rates.

Rate of CO₂ Regeneration: AMP vs MEA. To compare CO₂ regeneration rate between MEA and AMP, CO₂-saturated MEA and AMP solutions are prepared. The calculated saturation results for AMP and MEA revealed that after bubbling with CO₂, the molar ratio of solvent to CO₂ is approximately 1:1 when saturated using the standard procedure (consecutive absorption tests with a 15% CO₂ gas mixture until no further absorption is seen, then bubbling with pure CO₂ overnight). During regeneration, the packed absorber, used as the regenerator, is only heated to 93 °C, since in the present reactor setup, this is the highest temperature that can be safely maintained to prevent the water or solution from boiling. CO2-saturated AMP or MEA solution is sprayed on the top of the packing, while the CO₂ releasing rate is recorded with the aid of a bagmeter. The data in Table 3 show that CO2 releasing rate from AMP solution is about 80% faster than from MEA solution. No purge gas is used.

Parametrics Tests. The effects of height of the packed column and column temperature on CO₂ capture efficiency using 20 wt % MEA were evaluated. The height of packed column parameter varied from a minimum 18 cm to a maximum 71 cm; the column temperature study ranged from 29 to 54 °C. Sections of BX Gauze structured packing that were approximately 18 cm in length were used. An O-ring was inserted between adjacent structured packing to prevent liquid channeling along the wall of the packed column. The results are plotted in Figure 3. The molar ratio of MEA solution flowrate to CO₂ gas flow rate is 2.0. At a constant temperature, increasing the height of the packing increases the CO₂ removal. The relationship between the height and CO₂ removal is almost exponential. The increase in CO2 removal becomes marginal

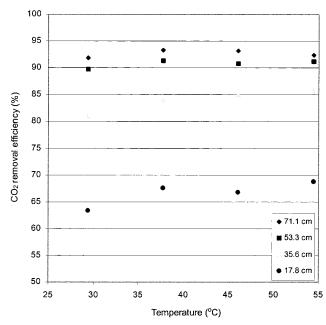


Figure 3. CO₂ removal efficiency vs temperature at various packing heights (20% MEA solution).

Table 4. Effect of Organic Diluent (methanol) on CO₂
Absorption by MEA Solution^a

test	MEA, wt %	methanol, wt %	water, wt %	density of overhead condensate, g/mL	CO ₂ removal efficiency, %
1	20	60	20	0.815	96.5
2	20	40	40	0.858	94.7
3	20	20	60	0.881	92.7
4	20	0	80	0.989	93.9

 $^{\it a}$ Absorber temperature: 37 °C; absorber height: 53 cm; mole MEA inlet/mole CO2 inlet: 2.0.

above a certain packed column height. The effect of reaction temperature on CO_2 removal efficiency is relatively insignificant in the range between 38 and 54 °C.

Effects of Organic Diluent. Although the assumption was made that organic diluents would reduce the energy requirements of regeneration, experiments were conducted to determine if the organic diluent would have any impact during the absorption step. Table 4 shows the effect of methanol on CO₂ absorption by MEA solution during testing. It indicates that if methanol is substituted for water, there is no appreciable difference in CO₂ absorption by MEA solution at 20%, 40%, and 60% methanol concentrations. However, the overhead methanol carryover was substantial. The fraction of methanol in the overhead condensate trap in the gas exit line was approximately calculated from the known density of pure methanol (0.79 g/mL), the measured density of the methanol-free MEA solution (0.99 g/mL), and the measured density of overhead condensate (0.82 g/mL) for the 60% (or at 0.6 fraction) methanol in MEA solution. The fraction of methanol in the overhead condensate was thus calculated at 0.89. The concentration of methanol increased from the original 60% in the MEA solution to 88.8% in the overhead condensate, an increase of 48%. The low boiling point of 64.7 °C for the methanol caused this preferential vapor carryover. Although, methanol would be unsuitable for use as an organic diluent in an atmospheric pressure application,

Table 5. Effect of Organic Diluent (ethylene glycol) on CO₂ Absorption by MEA Solution^a

test	MEA, wt %	ethylene glycol, wt %	water, wt %	density of overhead condensate, g/mL	CO ₂ removal efficiency, %
1	20	60	20	0.981	80.1
2	20	40	40	0.992	85.5
3	20	20	60	0.985	88.8
4	20	0	0	0.989	92.4

 a Absorber temperature: 37 °C; absorber height: 53 cm; mole MEA inlet/mole CO₂ inlet: 2.0.

it will be suitable in an higher pressure system, such as IGCC, since the high pressure raises the boiling point of the methanol.

The CO_2 solubility in methanol was also measured using the same packed column and only 5% CO_2 removal efficiency was obtained by pure methanol from the simulated flue gas.

Table 5 shows the effect of ethylene glycol on CO_2 absorption by MEA solution. In contrast to methanol, ethylene glycol as diluent suppresses CO_2 absorption by MEA solution. The higher the concentration of the diluent the lower the CO_2 removal efficiency. Also in contrast to methanol experiments, the density of overhead condensate stayed virtually unchanged at different diluent concentrations. This was not surprising, since pure ethylene glycol has a boiling point of 198 °C. This shows that ethylene glycol could be a viable organic diluent at atmospheric pressure. However, an economic study will dictate if the lower regeneration cost can more than compensate for the lower CO_2 removal efficiency of the chemical scrubbing system.

Conclusions

Investigations of amine-based scrubbing for CO₂ capture were performed to elucidate ways to improve this chemical absorption process. Increasing the gasliquid contacting area has a major impact on scrubbing. Absorption tests revealed that for a particular amine, structured packing improves the absorber efficiency and absorption rate as compared to the more traditional random packing. The type of amine is also a consideration. At the same bed geometry, the conventional MEA performed much better during absorption studies than the sterically hindered amine, AMP. However, in the regeneration step, the CO₂ releasing rate from the saturated AMP solution is over 80% greater than from saturated MEA solution. By extracting information from the above results, it can be speculated that if the more easily regenerable AMP is substituted for MEA, an overall process benefit will be obtained if a structured packing is used as compared to the random packing. Additionally, organic diluents can reduce the sensible heat duty in the regeneration step, but experimental results indicate that the volatility of the organic diluent and its impact on the absorption step are important considerations. Other techniques to improve the aminebased scrubbing will be investigated in the future.

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